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Clathrate hydrates in the system $\text{H}_2\text{O}-\text{Ar}$ at pressures and temperatures up to 30 kbar and 140 °C

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Studies of the binary mixture $\text{H}_2\text{O}-\text{Ar}$ —by means of a quasi-isochoric scanning method—have revealed the range of stability of clathrate hydrates in the high-pressure and high-temperature region. The results obtained show an extension of the decomposition curve above the melting curve of pure argon and up to the melting curve of pure ice VII. At low pressures the argon decomposition temperature first increases and then decreases with pressure, showing a local maximum and minimum temperature. At higher pressures the slope of the decomposition curve remains positive but undergoes three more breaks. Two new quadruple points have been determined; at 105 °C, 20 kbar (Q_4) and at 136 °C, 29 kbar (Q_5). In the lower region (below 10 kbar) the decomposition curve shows two breaks; at 31.5 °C, 6.2 kbar (Q_2) and at 37.5 °C, 9.6 kbar (Q_3), indicating that three different clathrate structures are formed in this region. The positions of the three-phase lines separating the two clathrate structures at lower pressure could be obtained via Raman spectroscopy since the pressure and temperature dependence of the vibrational frequencies of the coupled O–H oscillations is different for each clathrate structure. © 1999 American Institute of Physics. [S0021-9606(99)51945-4]

I. INTRODUCTION

Clathrate hydrates are a special class of inclusion compounds in which hydrogen bonded water molecules form a polyhedral cagelike structure (the host lattice) around nonpolar or weakly polar molecules (guests). In the case of argon, this solid phase can be formed above 88 bar (the pressure at the lowest quadruple point Q_1 (see Fig. 1) at temperatures above and below the melting line of ice but it does only occur in mixtures. Stability of clathrate hydrates requires a minimum occupancy of the cages by the guest molecules. The cages are stabilized by van der Waals forces¹ but the interaction with the guest molecules is very weak.

Each structure consists of two or more different fundamental cages. The structure to be formed depends mainly on the size of the guest molecule and is not strictly stoichiometric, in the sense that the composition is not strictly unique, since the fractional occupancy of the cages is somewhat dependent on pressure and temperature. The thermodynamic stability of clathrate hydrates has been explained by van der Waals and Platteeuw.² Clathrate hydrates have been extensively investigated experimentally^{3,4} and by using computer simulations.^{5,6} Recent studies include the crystal structure^{7,8} and the thermodynamic stability^{9,10} of clathrate hydrates.

The present study is concerned with the determination of the decomposition curve of argon clathrate hydrate and the three-phase lines separating the different clathrate structures. This system has been chosen for the comparison it allows with experiments on nitrogen hydrates;^{3,11} nitrogen and argon have about the same diameter but different orientational degrees of freedom. Also, the results of measurements up to 15 kbar by Dyadin *et al.*^{12,13} on several systems gave rise to

the expectation that argon clathrates might exist at relatively high pressures and temperatures.

II. EXPERIMENTAL METHODS

The experiments have been carried out with a diamond anvil cell (DAC) (Ref. 14) connected to a temperature control device.¹⁴ Under the microscope, the stainless steel 301 gasket was loaded with a droplet of deionized water and an air bubble. After mounting the cell in a pressure vessel, the air was purged and replaced by pure (99.999%) argon gas. On the basis of the size of the argon bubble, only a rough estimate of the composition could be made; all the sample mixtures used during the p – T scans had roughly the same composition (same bubble size) and contained much more water than argon.

To investigate the phase behavior three kinds of techniques have been used:

- (1) Quasi-isochoric scanning¹⁵ (p – T scans). In this way two-phase lines in pure systems and three-phase lines in binary mixtures can be detected by a discontinuity in the pressure or by a sudden increase of the pressure (pressure jump) if a sufficiently large volume change occurs. The p – T scan around the clathrate hydrate decomposition curve at about 15 kbar is shown in Fig. 2. The transition takes place gradually, so there is a range of pressures where the three phases coexist and the p – T plot follows the three-phase line.
- (2) Visual observation through a microscope (see Fig. 3). A phase transition can be detected visually by a change in the color, or structure (solid–solid transition) or by the melting of a solid phase (solid–liquid transition). At points on the transition line the pressure was measured.

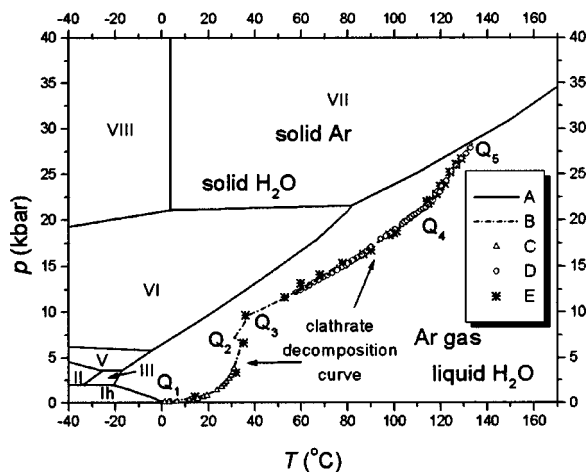


FIG. 1. p - T projection of the phase diagram for the water-argon system. (A) Pure H_2O transitions; (B) clathrate hydrate decomposition curve, Dyadin *et al.* (Ref. 12); (C) clathrate hydrate decomposition curve, Marshall *et al.* (Ref. 20); (D) p - T measurements of the clathrate hydrate decomposition curve, this work; (E) visual observation measurements, this work.

- (3) Determination of the vibrational spectrum of the molecules in the different clathrate regions.

For the p - T scans we used filling pressures of 200 bar. The DAC was mounted on a frame for further pressurization. The pressure in the DAC was determined using the ruby fluorescence technique with the scale of Mao *et al.*¹⁶ and the temperature correction of Vos and Schouten.¹⁷ The ruby was illuminated by the 488 nm line of an argon-ion laser at beam intensities of 1 mW. At pressures below 5 kbar the beam was passed through a gray filter to prevent heating of the chip. The ruby signal passes the entrance slit (100 μm) of a BM100 single monochromator and is detected by an Optical Multi Channel Analyzer. To avoid disturbance of the pressure measurement by plasma peaks a short wave pass filter was used.

First, the sample cell was pressurized and set at the desired temperature. After stabilization, the cell was heated in

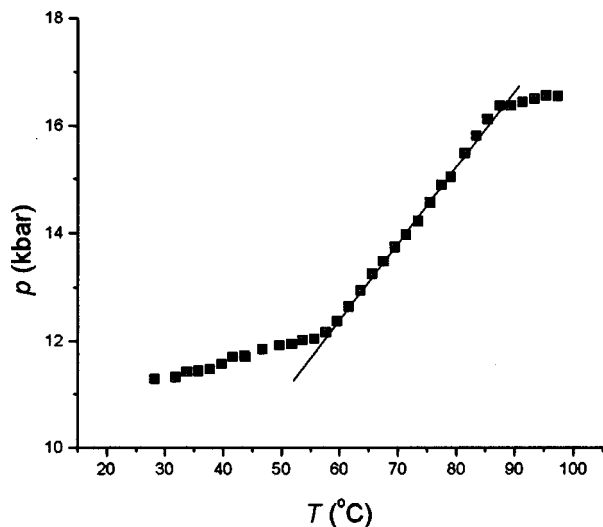


FIG. 2. p - T scan of the system $\text{H}_2\text{O}-\text{Ar}$; the solid line represents a part of the measured decomposition curve of argon clathrates.



FIG. 3. Image of the sample cell (diameter 200 μm) with the mixture $\text{Ar}-\text{H}_2\text{O}$ at about 90 $^{\circ}\text{C}$ and 20 kbar. The phases can be distinguished visually; the clathrate hydrate phase (left half of the cell; fairly transparent); the solid argon phase (in the upper right corner; darker); and the fluid phase (mainly at the top and the center of the cell; totally transparent). The dark spot at the bottom is the ruby chip.

steps of 2 $^{\circ}\text{C}$. Twenty minutes following each temperature step, the pressure was measured. Before and after each quasi-isochoric temperature scan the spectrograph was calibrated using the argon line at 696.54 nm, resulting in an accuracy of 0.1 cm^{-1} . The temperature was measured with a calibrated Copper-Constantan thermocouple with an uncertainty of 0.1 $^{\circ}\text{C}$. The absolute uncertainty in the pressure is estimated to be 0.3 kbar below room temperature and up to 0.5 kbar at temperatures up to 170 $^{\circ}\text{C}$. The relative accuracy, within one scan, is better (about 0.15 kbar). Note that, for all points on the decomposition curve, the mixture consists of a solid phase (or two solid phases) surrounded by a fluid (or fluid mixture). So, for all these points, pressure gradients can be excluded. Further, for all (other) measuring points, one of the phases is a clathrate. And since, during the formation of the clathrate, there is always a fluid present, also for these points, it is clear that there can be no pressure gradients.

For the visual method the same set up has been used. The cell was heated in steps of 1 $^{\circ}\text{C}$ with intervals of about 5 min. Only at points on the transition line the pressure was measured. In this case the accuracy also depends on the amount and the clarity of the solid involved and is generally less compared to p - T scans. Therefore this method has only been used at low pressures, when the volume change was not large enough to be measured with a quasi-isochoric scan, and also to give a quick indication about the position of the transitions.

The Raman experiments were performed using 400 mW of laser power. In order to reduce the liquid H_2O signal and to get the maximum amount of clathrate we used a filling pressure of 2 kbar for the argon gas.

TABLE I. Experimental data of the argon clathrate hydrate decomposition curve.

T (°C)	p (kbar)	T (°C)	p (kbar)	T (°C)	p (kbar)	T (°C)	p (kbar)	T (°C)	p (kbar)
57.69	12.16	77.52	14.88	88.21	16.62	107.54	20.35	118.71	23.13
59.65	12.37	79.13	15.03	90.23	17.09	108.59	20.57	119.75	23.07
61.63	12.64	81.53	15.47	94.28	17.95	109.57	20.69	120.51	23.63
63.63	12.94	83.53	15.80	96.38	18.25	110.61	20.86	122.52	24.25
65.65	13.25	85.46	16.10	98.44	18.54	111.66	21.08	124.81	25.31
67.59	13.48	87.48	16.36	100.51	18.96	112.60	21.23	126.88	25.89
69.56	13.74	80.07	15.26	103.47	19.55	113.66	21.38	128.90	26.68
71.46	13.97	82.08	15.61	104.49	19.80	114.70	21.64	130.99	27.24
73.54	14.22	84.09	15.91	105.55	19.90	116.75	22.12	132.91	27.87
75.59	14.56	86.21	16.24	106.50	20.16	117.77	22.84		

The detection system consists of a double monochromator (entrance slit 200 μm ; instrumental width 1.5 cm^{-1}) and a CCD detector. All measurements have been done in forward scattering. Before each measurement the spectrograph was calibrated, using the neon line at 576.44 nm. The Raman spectra of the coupled O–H oscillations of the two clathrate structures are dominated by the simultaneously present liquid water signal. For the determination of the main peak position of the clathrate spectra we used a Gaussian fit. But first, the part of the liquid water signal that overlapped the clathrate spectra was accounted for by fitting a linear function through points on both sides of the main clathrate peak and subtracting this linear fit from the signal. Of course, with this method the calculated frequency might be shifted with respect to the true value. Since the liquid H_2O signal does not change much as function of pressure¹⁸ and temperature¹⁹ and since the amount of clathrate and liquid H_2O is constant within a pressure scan, the subtraction will only introduce a relative error in the peak position. The goal of this investigation—the pressure and temperature dependence of the frequency—is hardly affected by this procedure.

III. RESULTS AND DISCUSSION

A. Determination of the clathrate hydrate decomposition curve

The results of a detailed study of the phase equilibria in the water–argon system at pressures between 3.4 and 30.5 kbar and temperatures between 14 and 140 °C are presented in Fig. 1 (and Table I) and are in good agreement with measurements up to 4 kbar by Marshall *et al.*²⁰ and up to 15 kbar by Dyadin *et al.*¹²

In the temperature range investigated (up to 200 °C and 30 kbar) the system water–argon shows a demixing of the fluid phase. At temperatures above the decomposition curve and pressures below the melting line of argon, two separate fluid phases are visible through the microscope; a liquid and a gas phase. The liquid phase is water rich and the gas phase is argon rich. In the low-pressure region the clathrate phase can be obtained from this liquid–gas phase. When the temperature is lowered down to the decomposition temperature, the formation of the clathrate is hindered by metastability of the liquid and gas phases. For example, although at about 4 kbar the clathrate hydrate is the stable phase below 32 °C, the sample has to be cooled much further and only at about 2 °C the hydrate forms.

In the region above 5 kbar the clathrate phase is only obtained from one of the ice phases; when cooling down from the liquid–gas equilibrium, ice VI or ice VII will form instead of clathrate. To obtain the clathrate phase the cell was heated from the ice region in question. At the ice–liquid transition the hydrate starts to form.

In the region below 10 kbar p – T scans have been performed at 2, 4, 6, and 8 kbar. None of those scans showed a pressure jump at the three-phase line clathrate–liquid–gas (L – C – G), although the clathrate phase was visible at the beginning of each scan. Results of Marshall *et al.*²⁰ showed a relatively small pressure jump of 14 bar at 500 bar. This is too small to be detected in a DAC. The relative uncertainty in the pressure is about 150 bar. So only pressure jumps of about 150 bar and larger can be detected. If the slope of the transition line in the p – T projection, $dp/dT = \Delta S/\Delta V$, is small, the change in the entropy ΔS is relatively small, or the volume change ΔV and thus the pressure jump is relatively large. Considering the small value of ΔV , the change in entropy at 500 bar must be very small. For the decomposition line between 4 and 8 kbar this need not be the case since the different slopes on both sides of the second and third quadruple points (Q_2 and Q_3) are much steeper in this area. At about 6 kbar the three-phase line shows a temperature maximum above which ΔV is probably even negative.

In the region above Q_3 the isochoric scanning method worked out very well and p – T scans at 12, 15, and 19 kbar revealed large pressure jumps of about 4 kbar. As a consequence, the volume change at the three-phase line in this area must be considerable, compared to lower pressures. Since the clathrate–gas equilibrium is transformed into the liquid–gas equilibrium, as in the low-pressure cases, this suggests that the density of the corresponding clathrate hydrate structure is higher than that of the low-pressure structures.

Above 20 kbar, i.e., above the new quadruple point (Q_4), the pressure jumps are less profound but still considerable; 2.5, 2.5, and 3 kbar at 21, 22, and 25 kbar. At 27 kbar the clathrate hydrate decomposition curve could not be detected with this method. Instead, starting in the ice VII region, the p – T plot follows the three-phase line related to the melting line of pure ice VII. In comparison with pure water, the transition line in the mixture is not shifted within experimental accuracy, as can be seen in Fig. 4 and we can conclude that argon does not dissolve or hardly dissolves in ice VII.

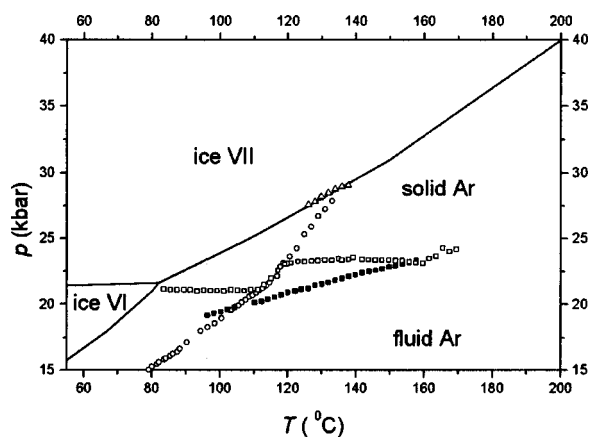


FIG. 4. Melting lines of the pure components and the corresponding three-phase lines in the mixture. Solid lines, phase diagram of pure water; open triangles, corresponding three-phase line liquid-ice VII-clathrate ($L-I_{\text{VII}}-C$) in the mixture; solid squares, melting line of pure Ar; open squares, $p-T$ measurements of corresponding three-phase line $L-G-S_{\text{Ar}}$ and of the clathrate decomposition curve in the mixture.

With the scan beginning at 21 kbar two phase transitions were detected; one at 110 °C, in a direct line with the clathrate decomposition curve and another one at 23 kbar and 160 °C. Now there are two possibilities:

- (1) The first transition line is the clathrate decomposition curve and the second is the three-phase line related to the melting line of pure argon; liquid-gas-solid argon ($L-G-S_{\text{Ar}}$).
- (2) The first transition line corresponds to a change in the clathrate hydrate structure and the second transition line is the extension of the decomposition curve of another new clathrate structure. In that case the three-phase line $L-G-S_{\text{Ar}}$ still has to be located.

To investigate the second possibility—another, new clathrate hydrate phase—several extra $p-T$ scans at higher pressures have been performed to detect the transition line $L-G-S_{\text{Ar}}$, but with no result. In addition, since in literature only measurements of the melting line of argon up to 18 kbar are mentioned, an extra $p-T$ scan has been performed with a sample of pure argon. The results are also plotted in Fig. 4 (full symbols). It is now clear that the second pressure jump indeed corresponds to the argon melting line and again, because there is no shift, we may conclude that, at the most, a very low solubility of water in argon occurs.

On the basis of these results the new quadruple points $L-C-G-S_{\text{Ar}}$ (Q_4) and $L-I_{\text{VII}}-C-S_{\text{Ar}}$ (Q_5) can be positioned at 105 °C, 20 kbar and 136 °C, 29 kbar, respectively. Figures 5(a) and 5(b) show the schematic $T-x$ cross sections just below and above Q_4 . For simplicity's sake, the argon mole fraction of the clathrate structure indicated in the figures is fixed at about 0.15. On the liquid-gas transitions no quantitative data are available.

In cross sections just below the quadruple point pressure, the three-phase lines $C-G-S_{\text{Ar}}$ and $L-C-G$ are the borderlines of the $C+G$ area, respectively, below and above this region. Looking at cross sections even closer to Q_4 the three-phase lines move towards each other and up to higher tem-

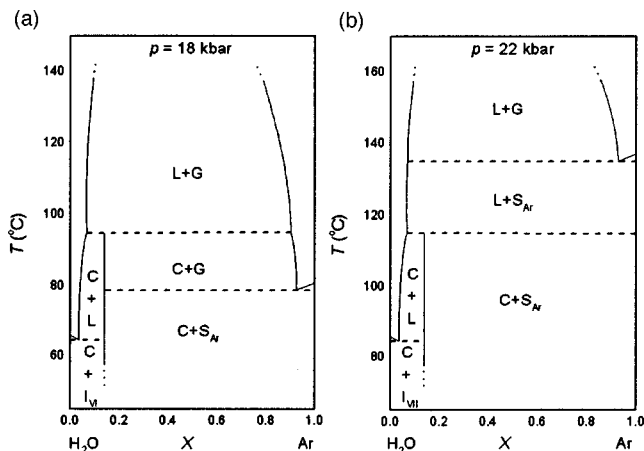


FIG. 5. (a) and (b) Cross sections of the $p-T-x$ diagram at constant pressures just below and above the quadruple point Q_4 .

peratures until they coincide at the quadruple point. Meanwhile the area $C+G$ becomes smaller and vanishes in Q_4 . In cross sections at pressures just above Q_4 a new area forms; $L+S_{\text{Ar}}$ marked by two new three-phase lines: $L-C-S_{\text{Ar}}$ below and $L-G-S_{\text{Ar}}$ above the new area. The same can be said about cross sections at constant temperature below the quadruple point. Only now the marking three-phase lines have changed places: the upper phase line is now the lower one and vice versa.

The fact that the remaining three-phase line ($C-G-S_{\text{Ar}}$) emanating from Q_4 could not be detected with the scanning method nor by visual observation—although the starting point for all experiments was the ice boundary—is an indication for the composition of the mixture; from Figs. 5(a) and 5(b) it is clear that, for all the mixtures with argon filling pressures of 200 bar, the argon mole fraction must be small; for mixtures with argon mole fractions less than 0.15 the transition $C-G-S_{\text{Ar}}$ does not exist and for fractions a little higher than 0.15 the amount of argon that melts at the transition line results in a pressure change too small to be detected.

B. Raman investigations and clathrate structures

In Fig. 6 the part of the $p-T$ projection of the phase diagram is shown with quadruple points Q_2 and Q_3 positioned at the two breaks;¹² 31.5 °C, 7.2 kbar and 37.5 °C, 9.6 kbar. Given that a quadruple point is the point of intersection of four three-phase lines and the fact that both argon and water are in the fluid phase in this region, this is an indication that there must be three different clathrate types in this area with separating three-phase lines at the lower break Q_2 ; $L-G-C_1$ and $L-G-C_2$ (the decomposition curves), C_1-C_2-G and C_1-C_2-L (the transition lines that mark the clathrate types). The remaining transition lines starting at the upper break Q_3 are C_2-C_3-L , C_2-C_3-G , and $L-G-C_3$.

The three-phase lines that separate the different clathrate types could not be detected by isochoric $p-T$ scanning, again as a result of the small pressure change at the transition, but through the microscope rearrangement and formation of small pieces of solid could be observed (although not

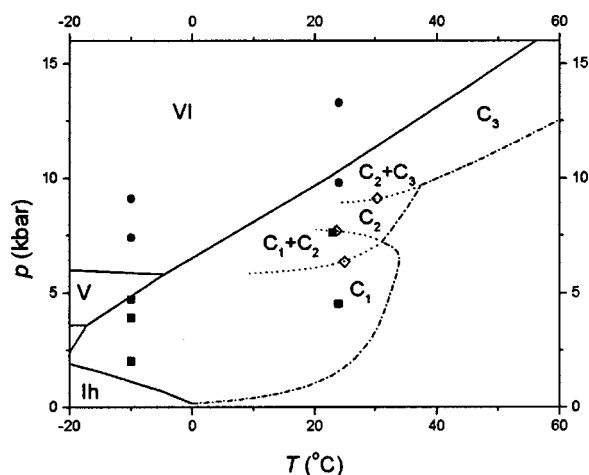


FIG. 6. p - T projection of the phase diagram. Squares, Raman measurements, structure C_1 ; circles, Raman measurements, structure C_2 .

very clearly); the points obtained are denoted with a diamond in Fig. 6. The proposed locations of three of the transition lines are indicated with dotted lines. The upper transition line marking the $C_2 + C_3$ and C_3 areas could not be detected this way.

The Raman spectra of C_1 and C_2 have more or less the same shape, as can be seen in Fig. 7. Therefore, the only indication for a structural transition is a small frequency shift and a change in the slope of the ν - p plot. The pressure and temperature dependence of the vibrational frequencies of C_1 and C_2 have been determined for the range from 2 to 14 kbar and -10 to 24°C (see Fig. 8) and are, respectively, $-10 \pm 0.5 \text{ cm}^{-1}/\text{kbar}$ and $0.95 \pm 0.05 \text{ cm}^{-1}/\text{K}$ for C_1 and $-4.5 \pm 0.2 \text{ cm}^{-1}/\text{kbar}$ and $0.90 \pm 0.02 \text{ cm}^{-1}/\text{K}$ for C_2 . The slopes of the fits are assumed to be independent of temperature. Due to the weakening intensity with increasing pressure and temperature the C_3 signal could not be detected.

About the possibility of the formation of an amorphous phase in this p - T region the following can be said. First of all there is no indication for yet another quadruple point between Q_3 and Q_4 or between Q_4 and Q_5 . This means that

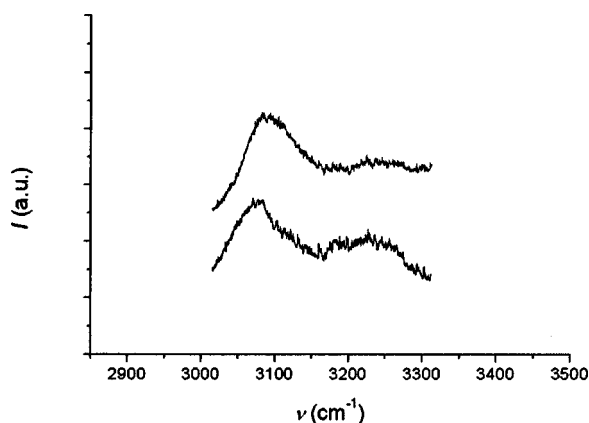


FIG. 7. Combined Raman spectra of the O-H stretching vibrations at -10°C in both, the liquid phase and the clathrate phase. Upper signal, 4.7 kbar, C_1 main peak at 3089 cm^{-1} , lower signal, 7.4 kbar, C_2 main peak at 3077 cm^{-1} .

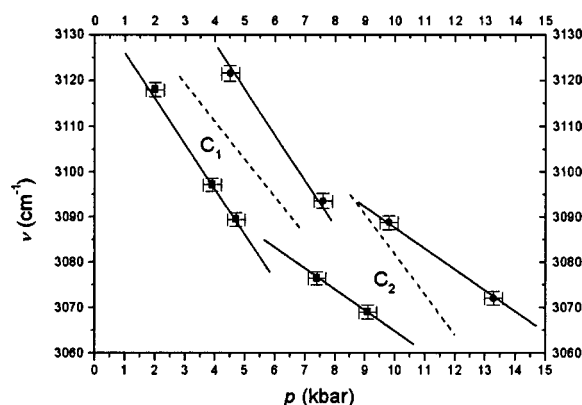


FIG. 8. Peak positions of the O-H stretching vibrations in the clathrate structures C_1 and C_2 at -10°C (squares) and 24°C (circles); this work. The dashed lines represent measurements by Van Hinsberg (Ref. 11) on nitrogen clathrate hydrates at room temperature.

in case of any amorphous (mixed) phase, the third clathrate structure C_3 would not exist and would actually be the amorphous phase. So, up from Q_3 we then would have measured the decomposition curve of the amorphous phase. But this is very unlikely, since the determination of the three phase line is reproducible for different compositions. Further, the mentioned phase is formed out of a solid (ice) during heating via melting at the melting line of ice and not out of a fluid (amorphous) phase during cooling. So all together, although the C_3 signal could not be found in this p - T region, we have no indication of the formation of an amorphous phase.

It is interesting to compare these results with experiments on the mixture $\text{H}_2\text{O}-\text{N}_2$ by van Hinsberg *et al.*,^{3,11} because argon and nitrogen have almost the same diameter (3.85 and 4.09 Å). In the low-pressure range up to 9 kbar the clathrate decomposition curves in both systems show much resemblance. Both systems are assumed to form CS-II in the low-pressure region²¹⁻²³ (for the argon-water system this has been confirmed experimentally) and are assumed to form CS-I in the area between the second and the third quadruple point.^{12,21,24} Also, for both systems, the pressure at the local temperature maximum and the pressure at the second quadruple point is roughly the same, as is the slope above Q_2 up to 9 kbar. The important difference is that, for nitrogen hydrates, the decomposition curve is slightly shifted to higher temperatures. This could be due to the small difference in diameter. After all, the volume in the clathrate phase is the same for both, since in both cases CS-II is formed and because the molar volume of nitrogen in the fluid phase is larger, therefore the volume change ΔV at the transition must be somewhat larger in the nitrogen system. This implies a somewhat smaller slope of the transition line in the nitrogen case and, as a result, a shift to higher temperatures compared to the argon system.

At higher pressures, above Q_2 , the location of the transitions is quite different. Whereas in the nitrogen case the curve goes up rather steeply and intersects the ice VI melting line at 14 kbar (Q_3), the decomposition curve in the argon system also increases steeply up to 10 kbar (Q_3) but then the curve moves up to much higher temperatures, intersecting

the argon melting line at 20 kbar (Q_4) and intersecting the ice VII melting line at 29 kbar (Q_5). Considering the much larger volume change above 10 kbar, this significant difference in phase behavior can be explained by a much denser clathrate phase or an increase in argon concentration in the clathrate phase. The rotation of nitrogen, which is less spherical, is probably frustrated in the clathrate phase at higher pressures, resulting in a lower concentration. Because of this the dissociation temperature is expected to be lower and the change in entropy ΔS at the transition is expected to be larger. Therefore the slope must be steeper in the nitrogen system.

The shape of the Raman spectra of the coupled O–H oscillations of the water molecule in C_1 and C_2 in the two systems is very much the same. The vibrational frequencies of C_1 are a little shifted compared to those of the nitrogen system (see Fig. 8) but the pressure dependence is roughly the same. In the nitrogen system,¹¹ the pressure dependence of O–H stretching frequencies for both clathrates is almost equal; $-8.2 \text{ cm}^{-1}/\text{kbar}$ for C_1 and $-8.9 \text{ cm}^{-1}/\text{kbar}$ for C_2 . Further, the main peak position in C_2 is shifted 20 cm^{-1} upwards compared to that in C_1 , whereas in the argon system the shift in the main peak position is not constant because the pressure dependence of the frequency is quite different for C_1 and C_2 . Summarizing, we can conclude that the C_2 lattice in argon clathrates is less compressible than the C_2 lattice in nitrogen clathrates. This is remarkable, since in both cases CS–I is assumed and because the diameter of nitrogen is a little larger than that of argon.

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